Method for Producing a Shoe

Ins A1

This invention relates to a process for making shoes, more particularly sports shoes (so-called "trainers"), or individual components of shoes in which the components of the shoe, more particularly the upper and the outer sole, are joined together by bonding and at least one of the surfaces to be bonded is pretreated before application of the adhesive.

In shoe production, many individual components of the shoe are joined together by bonding. This applies in particular to trainers which are made solely by bonding. The bonds, more particularly the adhesive bond between the upper and the outer sole, are exposed to severe stressing in use and, accordingly, have to satisfy a number of requirements. Thus, they are expected to withstand strong forces during the use of the shoe and to be thermally stable at temperatures of up to about 80°C. High flexibility and hydrolysis stability, i.e. resistance to rainwater from outside and perspiration from inside, are further requirements.

A number of different plastics are used in modern shoes. Many of them are difficult to bond with the desired adhesives.

With some of the plastics, bondability is also reduced by the additives of which some migrate from the interior to the surface of the plastic and, in doing so, additionally impair bondability. Such additives include lubricants, such as fatty acid amides, or the silicone oils or stearates used as mold release agents in the injection molding process. Another reason for the poor bondability of some plastics is to be found in their nonpolar surfaces when a polar adhesive, such as a polyurethane-based adhesive for example, is to be used. It is clear from these few examples that poor bondability in each of the many combinations of a certain plastic and a certain adhesive can have different causes.

In the prior art, adhesion is improved by pretreating the surfaces to

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be bonded before application of the adhesive. To this end, it is known that the surfaces can be manually or automatically roughened with a milling tool or washed with a solvent and that, in addition, a halogenated substance can be applied and, after drying, reacts with the plastic surface and modifies it in such a way that better adhesion is achieved. The application of such a primer has many serious disadvantages. The substances are generally hazardous to health so that personnel have to be appropriately protected at considerable expense. Application, drying and reaction take a long time, require special workplaces and are relatively labor-intensive.

It is known from French patent application **FR 2 692 276 A1** (Bostik) that a solution of a chlorinated polymer containing an organic titanate can be used as primer. After application, the solution is activated by an energy source which may be ultraviolet radiation, an electron gun or a plasma or a corona treatment. This is intended to produce a reaction between the primer and the surface of the plastic to improve its adhesion. A particular example cited in the document in question is the bonding of synthetic rubber or elastomers in the shoe industry. The disadvantage of this process is that it again involves the use of a primer with all the attendant disadvantages as mentioned above. This is because adhesion is not improved by the action of the energy source, but instead by the reaction of the primer with the plastic surface. The energy source merely activates the primer.

It is known that the adhesion of plastic surfaces to be bonded in general can be improved by passing a concentrated plasma jet over the surface (**EP 0 761 415 A2**, Agrodyn Hochspannungstechnik GmbH). Particular reference is made here to the pretreatment of plastic films. Plastics in general, highly fluorinated polymers, for example PTFE, and metal surfaces, for example aluminium, are mentioned as the surfaces to be treated.

The plasma jet mentioned is produced by blowing a working gas,

more particularly air, through an electric arc at normal temperature and pressure. The so-called plasma jet is obtained as the working gas leaves the arc. It is not certain whether this plasma jet is actually a plasma in the true sense, i.e. a gas split at least partly into ions and electrons. However, it is crucially important that this jet is suitable for the pretreatment of plastic surfaces.

Instead of the concentrated plasma jet mentioned, which enables the surface to be pretreated at particular spots, a number of circularly arranged plasma jets rotating about the centre of the circle may also be used (**DE 298 05 999 U1**). An annular plasma jet is obtained in this way and may be used to rapidly sweep over and thus pretreat a relatively large surface.

However, if this process is used to bond a typical shoe sole material, i.e. synthetic rubber, adhesion is not significantly improved using the known process so that the earlier pretreatment processes mentioned above have to be applied.

Accordingly, the problem addressed by the present invention was to save steps in the process mentioned at the beginning while keeping investment costs to a minimum and avoiding the use of solvents as far as possible. In addition, only the surface to be bonded would be pretreated in the pretreatment and handling would be simple. The pretreatment process would lend itself to continuous and automated operation. The machinery used would take up little space so that existing production lines could easily be modified.

According to the invention, the solution to the problem stated above is achieved by the process mentioned at the beginning providing a plasma jet is produced under normal pressure and the surface to be bonded is pretreated with the jet. To this end, the plasma jet is directed onto the surface and, in particular, is moved over the surface.

It has surprisingly been found that, with certain sole materials, more

particularly ethylene/vinyl acetate, hereinafter referred to in short as EVA, and thermoplastic rubber, hereinafter referred to in short as TR, such effective pretreatment is possible that there is little, if any, need to use the usual primers. The process according to the invention may be carried out using the plasma jet described in EP 0 761 415 A2 or in DE 298 05 999 U1.

The linear plasma jet described in DE 298 05 999 U1 is preferably used because, in the pretreatment of outer soles for example, it enables the entire sole surface to be uniformly irradiated without the edges of the sole being pretreated. If, by contrast, a single fixed plasma jet is used, the surface to be bonded is more locally pretreated.

It is also important in the process according to the invention that only the required part of the surface rather than the entire surface of the workpiece is pretreated. This advantage is particularly apparent in the pretreatment of outer soles. Since the side edges of the sole are not pretreated, any excess adhesive on those edges may readily be removed after bonding because the edges of the sole show minimal adhesion. This advantage is particularly important where the adhesive is applied by spraying.

In a particularly preferred embodiment of the invention, the surface of foamed ethylene/vinyl acetate cut from a block ("diecut EVA") is pretreated exclusively with the plasma jet. It has been found that there is no need for an additional treatment with solvents or primers. After the plasma treatment, the adhesive, for example a reactive hotmelt, can still be applied after 14 days without any deterioration in the quality of the bond. In a tear test, failure occurs in the ethylene/vinyl acetate and not in the adhesive.

By contrast, in the prior art, the EVA has to be washed or roughened, treated with a primer and dried. If a hotmelt adhesive is used, the EVA also has to be preheated in a final step. According to the present

invention, these steps are now no longer necessary.

In another preferred embodiment of the invention, the surface of thermoplastic rubber is pretreated solely with the plasma jet and the adhesive is applied to the optionally preheated surface. Preheating of the surface is only necessary where hotmelts are used. Here, the adhesive may be applied immediately after treatment of the surface with the plasma jet because the surface is still warm then. If the adhesive is to be applied later, the surface should be additionally preheated before application. Further pretreatment measures are not necessary.

By contrast, in the prior art, this material has to be treated with a halogenated solvent or a corresponding gas and with a primer containing polyurethane in a solvent.

Finally, in another preferred embodiment, the surface of injection-molded foamed ethylene/vinyl acetate - for the pretreatment - is first roughened mechanically or with a solvent or is made to swell. The surface is then treated with the plasma jet. In this case, the relatively smooth surface has to be partly roughened before the plasma treatment. Organic solvents or alkaline solutions may be used as the solvent. After the plasma treatment, the adhesive, for example the reactive hotmelt, may be applied.

By contrast, in the prior art, the surface has to be washed with a solvent and coated with a UV primer, exposed to UV light and, finally, coated with a primer containing polyurethane in a solvent. According to the invention, no solvent is used and two process steps can be saved.

The invention is illustrated in the following by Examples and Comparison Examples. The process according to the invention was applied to the following exemplary materials, each test being carried out several times.

1 to 3) Various diecut EVA sole materials (manufacturer: Pou Chen) used as middle sole in the manufacture of Nike, Reebok and Adidas trainers.

4) TR sole material (standard test material based on

styrene/butadiene/styrene rubber [SBSR] of the PFI (Prüf- und Forschungsinstitut für die Schuhherstellung e.V.)

5) Foamed injection-molded EVA outer soles (manufacturer: Fu Tai) used in the manufacture of New Balance trainers.

Test specimens 120 mm long and 30 mm wide were diecut from these test materials. The surface of the test specimens was pretreated solely by normal-pressure plasma, i.e. was not subjected to any other pretreatment. The PlasmaTreat® plasma pretreatment system (manufacturer: Agrodyn Hochspannungstechnik GmbH) was used. The treatment was carried out using an RD 1013 rotation unit, an FG 1001 generator and an HTR 2001 high-tension transformer.

Parameters:	voltage:	300 V
	current:	11 A
	pressure:	2 bar (“working air”)

The distance between the surface to be treated and the exit opening of the plasma jet from the RD 1013 rotation unit was 10 mm. Only in the case of the injection-moulded foamed EVA materials was the surface additionally roughened by abrasion before the plasma treatment in another test.

The test bonding of these pretreated materials was carried out to DIN ES (European Standard) 522 (adhesives for leather and shoe materials, strength of the bonds) and DIN ES 1392 (Solvent-based and dispersion adhesives, tests for measuring the strength of bonds under defined conditions) against test leather (double chrome leather standard test material of the Satra Institute). The adhesive used was Macroplast QR 8116 (Henkel KGaA), a reactive polyurethane hotmelt specially developed for bonding soles). This adhesive was applied to the entire surface of the substrates from a slot die, the surface temperature being ca. 60°C, and

was activated, set and pressed to ES 1392.

Bond strength was tested by carrying out peel tests using a PFI tensile tester. To this end, the above-mentioned bonds were clamped in the tester and pulled apart at an angle of 180° and at a speed of 100 mm/min. The forces required for separating the bond in the peel tests were recorded and averaged after the measurement.

The results are set out in the following Table:

No.	Material	Pretreatment	Peel Force	Failure Pattern
1)	Diecut EVA (Nike)	None Plasma	< 1 N/mm 3.5 N/mm	Adhesion failure EVA failure
2)	Diecut EVA (Reebok)	None Plasma	< 1 N/mm 4 N/mm	Adhesion failure EVA failure
3)	Diecut EVA (Adidas)	None Plasma	< 1 N/mm 3.5 N/mm	Adhesion failure EVA failure
4)	TR (PFI test material)	None Plasma	1.5 N/mm 8-11 N/mm	Adhesion failure TR failure
5)	Foamed EVA (New Balance)	None Plasma Roughened + plasma	< 1 N/mm 1 N/mm 3.5 N/mm	Adhesion failure Adhesion failure EVA failure